

# Determination of Formal Oxidation State of Co in MBE-Grown Co-doped TiO<sub>2</sub>(001) Anatase Epitaxial Films by X-ray Absorption Spectroscopy

S.A. Chambers<sup>1</sup>, T. Droubay<sup>1</sup>, S. Thevuthasan<sup>1</sup>, N.H. Hamdan<sup>2</sup>

<sup>1</sup>Fundamental Science Division, Pacific Northwest National Laboratory  
Richland, WA 99352, U.S.A.

<sup>2</sup>Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.A.

## INTRODUCTION

Diluted magnetic semiconductors (DMS) consist of nonmagnetic semiconducting materials doped with a few atomic percent of impurity magnetic cations. Magnetic coupling occurs by virtue of exchange interactions between the magnetic spins and free carriers in the semiconductor. The interaction can occur via *p-d* or *d-d* exchange, and can lead to antiferromagnetic or ferromagnetic coupling, depending on the concentration and the local structural environment of the magnetic impurity. DMS materials grown as thin epitaxial films can be used as spin injectors for semiconductor heterostructures, provided they are ferromagnetic.

Virtually all conventional DMS materials exhibit Curie temperatures of ~100K or less and must be *p*-type, which means that the exchange interaction leading to ferromagnetic behavior is hole mediated. Most of the effort expended to date on understanding the crystal growth and properties of thin-film DMS materials has focused on Mn-doped II-VI, III-V, and Group IV semiconductors.<sup>1-4</sup> Relatively little effort has gone into the investigation of “nontraditional” semiconductors, such as semiconducting oxides, to see if they are more robust magnetically. However, one such oxide - Co-doped TiO<sub>2</sub> anatase (Co<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub>) - has recently been discovered to be the most magnetically robust DMS with regard to magnetic moment at saturation, coercivity, remanence, and Curie temperature.<sup>5</sup> Indeed, it is one of the very few DMS materials demonstrated to exhibit ferromagnetic behavior above 300K. In addition, it has been shown that the material can be grown epitaxially by both pulsed laser deposition (PLD)<sup>6</sup> and oxygen plasma assisted molecular beam epitaxy (OPA-MBE)<sup>5</sup> on SrTiO<sub>3</sub>(001) and LaAlO<sub>3</sub>(001). However, the resulting magnetic properties differed considerably for the two growth methods, with significantly better properties exhibited by OPA-MBE grown material.

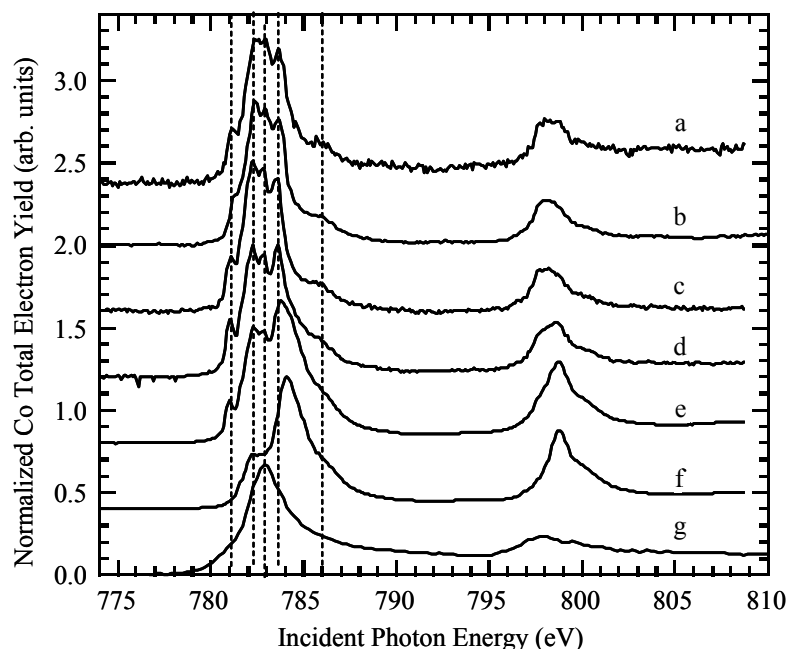
In order to understand the mechanism of magnetism in this fascinating material, it is essential to know the charge state of the magnetic cation (Co), and the doping type. We have utilized Co L-edge x-ray absorption spectroscopy (XAS) at beamline 9.3.2 to determine the Co charge state.

## EXPERIMENT

Epitaxial Co<sub>x</sub>Ti<sub>1-x</sub>O<sub>2-x</sub> films of high structural quality were grown by OPA-MBE on LaAlO<sub>3</sub>(001)<sup>7</sup> using a system at PNNL described in detail elsewhere.<sup>8</sup> The resulting samples were then transferred through air to beamline 9.3.2 and XAS measurements were made in total electron yield mode at the Co L-edge, Ti L-edge, and O K-edge. X-ray absorption near-edge spectra (XANES) were also recorded for several Co standards for comparison purposes. No surface cleaning was done, as the distribution of Co has been shown to be strongly modified by post-growth annealing at the temperatures required to rid the surface of carbon, or remove sputter damage.

## RESULTS

We show in Fig. 1 Co L-edge XAS data for three films with different Co mole fractions ( $x$ ) (Fig. 1a-c), and for standards containing Co in different oxidation states and local structural environments (Fig. 1d-g). The  $\text{CoTiO}_3$  standard was a powder,  $\text{CoO}$  was a (001)-oriented bulk single crystal,  $\gamma\text{-Co}_2\text{O}_3$  was a 100 nm thick (001)-oriented epitaxial film grown on  $\text{MgO}(001)$  at PNNL, and the Co metal standard was a polycrystalline film evaporated *in situ* in the XAS chamber. Comparison of all film spectra with those for the standards reveals a good fit with both  $\text{CoTiO}_3$  and  $\text{CoO}$ , which both contain  $\text{Co}^{+2}$ , but a very poor fit for both  $\gamma\text{-Co}_2\text{O}_3$ , which contains  $\text{Co}^{+3}$ , and for Co metal. The fit to  $\text{CoTiO}_3$  is better than that to  $\text{CoO}$ . However, there is some similarity between the reference spectra for  $\text{CoO}$  and  $\gamma\text{-Co}_2\text{O}_3$ , particularly in the vicinity of the feature at 784 eV. This result indicates that there may be some  $\text{Co}^{+3}$  in the  $\text{CoO}$  single crystal. The very high degree of similarity between the spectra for the Co-doped anatase films and the  $\text{CoTiO}_3$  standard establishes that Co in the former is in the +2 formal oxidation state. Interestingly, using the Co evaporation rate and oxygen plasma beam intensity we have used for the growth of  $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$  result in the epitaxial growth of metastable  $\gamma\text{-Co}_2\text{O}_3$  on  $\text{MgO}(001)$ . Therefore, the anatase lattice stabilizes the formation of  $\text{Co(II)}$ , even though the conditions would result in  $\text{Co(III)}$  formation if pure Co oxide were allowed to grow under comparable



conditions.

Fig. 1 Co L-edge XAS for 20 nm thick films of epitaxial  $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$  on  $\text{LaAlO}_3(001)$ : (a)  $x = 0.01$ , (b)  $x = 0.06$ , (c)  $x = 0.08$ . Also shown are spectra for reference compounds containing Co in different formal oxidation states: (d)  $\text{CoTiO}_3$ , (e)  $\text{CoO}$ , (f)  $\gamma\text{-Co}_2\text{O}_3$ , and (g) Co metal.

## SIGNIFICANCE

Ion channeling measurements conducted at PNNL reveals that Co substitutes for Ti in the anatase lattice. Furthermore, Hall effect measurements carried out at PNNL show that these films are *n*-type semiconductors as grown, despite the fact that no intentional *n*-type doping was carried out. The origin of the *n*-type doping may have to do with the presence of H in the film,

which has been detected by  $^{19}\text{F}$  nuclear reaction analysis at PNNL at a concentration that is of the same order of magnitude as that of the free carriers –  $10^{19}$  to  $10^{20} \text{ cm}^{-3}$ . H may be the direct dopant, as occurs in  $n\text{-ZnO}$ .<sup>9</sup> Alternatively,  $\text{H}_2$ , which is present in the growth chamber at a very low partial pressure, may partially reduce lattice oxygen during growth to produce OH and a free donor electron according to the reaction  $\text{O}^{2-}_{(\text{lattice})} + (1/2)\text{H}_2 \rightarrow \text{OH}^{-}_{(\text{lattice})} + \text{e}^{-}$ . This phenomenon is currently under more detailed investigation.

It thus appears that Co-doped anatase  $\text{TiO}_2$  is ferromagnetic by virtue of *electron* mediated exchange interaction between  $\text{Co}^{+2}$  cations that substitute for  $\text{Ti}^{+4}$  in the lattice. In order to maintain charge neutrality, each substitutional  $\text{Co}^{+2}$  must be accompanied by an  $\text{O}^{2-}$  vacancy. However, such vacancies are uncharged and therefore do not contribute any donor electrons. In fact,  $n$ -type semiconducting behavior and Co substitution are independent phenomena; some highly resistive films are nonmagnetic despite having several at. % Co. Indeed, the magnetization depends as much on the free carrier concentration as on the presence of substitutional Co, as expected for a DMS.

Significantly, virtually all other known DMS materials are ferromagnetic by virtue of *hole* mediated exchange interaction, which has been thought to be the stronger interaction.<sup>10</sup> Therefore, Co-doped  $\text{TiO}_2$  anatase is a highly unusual and potentially very important DMS in that it exhibits strong electron mediated exchange interaction at temperatures of at least 500K. No other known DMS exhibits these properties.

## REFERENCES

1. R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, L.W. Molenkamp, *Nature* **402**, 787 (1999).
2. B.T. Jonker, Y.D. Park, B.R. Bennett, H.D. Cheong, G. Kioseoglou, A. Petrou, *Phys. Rev. B* **62**, 8180 (2000).
3. R.K. Kawakami, Y. Kato, M. Hanson, I. Malajovich, J.M. Stephens, E. Johnston-Halperin, G. Salis, A.C. Gossard, D.D. Awschalom, *Science* **294**, 131 (2001).
4. Y.D. Park, A.T. Hanbicki, S.C. Irwin, C.S. Hellberg, J.M. Sullivan, J.E. Mattson, T.F. Ambrose, A. Wilson, G. Spanos, B.T. Jonker, *Science* **295**, 651 (2002).
5. S.A. Chambers, S. Thevuthasan, R.F.C. Farrow, R.F. Marks, J.-U. Thiele, L. Folks, M.G. Samant, A.J. Kellock, N. Ruzyski, D.L. Ederer, U. Diebold, *Appl. Phys. Lett.* **79**, 3467 (2001), and, S.A. Chambers, *Mat. Today*, to appear, April issue (2002).
6. Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S.-Y. Koshihara, H. Koinuma, *Science* **291**, 854 (2001).
7. S.A. Chambers, C. Wang, S. Thevuthasan, T. Droubay, D.E. McCready, A.S. Lea, V. Shutthanandan, C.F. Windisch, Jr., submitted to *Thin Solid Films* (2002).
8. S.A. Chambers, *Surf. Sci. Rep.* **39**, 105 (2000).
9. D.M. Hofman, A. Hofstaetter, F. Lieter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, and P.G. Baranov, *Phys. Rev. Lett.* **88**, 045504-1 (2002).
10. T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, *Science* **287**, 1019 (2000).

The work was funded by a Laboratory Directed Research and Development grant associated with the PNNL Nanoscience and Technology Initiative, and by DOE BES Materials Science.

Principal Investigator – S.A. Chambers. Phone – (509) 376-1766. E-mail – sa.chambers@pnl.gov